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Inertia tensor and size of a polymer chain

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Abstract. Guided by an approach used in the study of membranes we construct the partition function for a discrete Gaussian chain model of polymers. The Hamiltonian is $\mathcal{H} = \mathcal{H}_0 + \mu \operatorname{tr} \mathcal{T}$, where $\mathcal{H}_0$ describes the chain connectivity, $\mathcal{T}$ is the inertia tensor, which gives the shape and size of the polymer chain, and tr denotes the trace. Here we consider only the size, $R_G^2 = \langle \operatorname{tr} \mathcal{T} \rangle$, which is obtained from the partition function by differentiating with respect to the conjugate variable μ. The partition function is expressed in terms of the hypergeometric function ${}_2F_1(n+1, -n+1; \frac{3}{2}; -z^2)$, an orthogonal polynomial, where n is the number of monomers and z^2 is the ratio of μ and the coefficient in $\mathcal{H}_0$. The limit $z \to 0$ corresponds to the random coil, while the limit $z \to 1$ describes a compact object. We also study the excluded volume problem by discretizing Edwards' continuous self-avoidance term. We obtain dimensionally regularized expressions for the radius of gyration and the end-to-end distance. The short distance cut-off dependence of the continuous model is reproduced.

1. Introduction

A commonly used measure of the size of a flexible polymer chain in solution is its end-to-end distance R_E. However, it was recognized long ago [1] that the radius of gyration R_G is a better measure of the size than R_E. Indeed the structure (or form) factor

$$G(\boldsymbol{k}) = \frac{1}{n}\left\langle \sum_{\ell,m=1}^{n} \exp(\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{r}_\ell - \boldsymbol{r}_m)) \right\rangle \qquad |\boldsymbol{k}| = (4\pi/\lambda)\sin(\theta/2) \tag{1.1}$$

which is proportional to the intensity of scattered radiation [2, 3], is determined by the radius of gyration through the relation $G(\boldsymbol{k}) = nf(|\boldsymbol{k}|R_G)$ [2, 3]. Here n is the number of links in the chain, θ is the scattering angle, and λ is the wavelength of the radiation.

Despite the realization that R_G is more fundamental than R_E, most theoretical studies take the end-to-end distance (which is not accessible to experiment) as a central object, and determine the radius of gyration on that basis. This is due in part to the fact that the end-to-end distance of a chain (or segment thereof) has a Gaussian distribution when the number of links (or monomers) is sufficiently large; the distribution of R_G is not known [1]. In this approach one calculates the Fourier transform

$$C(\boldsymbol{k}; x_1, x_2) = \langle \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{r}(x_1) - \boldsymbol{r}(x_2)]} \rangle \tag{1.2}$$

of the probability distribution $P([\boldsymbol{r}(x_1) - \boldsymbol{r}(x_2)] - \boldsymbol{\rho})$ for two links located at positions x_1 and x_2, respectively, along the chain, to be separated by a distance $\boldsymbol{\rho}$. The braces $\langle\ \rangle$ denote an average, and the position in the embedding space of monomer i is denoted by $\boldsymbol{r}(x_i)$. The segment end-to-end distance

$$\langle |\boldsymbol{r}(x_1) - \boldsymbol{r}(x_2)|^2 \rangle = -[\nabla_k^2 C]|_{k=0} \tag{1.3}$$

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is then used to calculate the radius of gyration,

$$R_G^2 = \frac{1}{L}\iint \mathrm{d}x_1\,\mathrm{d}x_2\langle[\boldsymbol{r}(x_1)-\boldsymbol{r}(x_2)]^2\rangle \tag{1.4}$$

where L is the contour length of the chain. Thus calculation of R_G^2 is, in a sense, based on the end-to-end distance $\langle|\boldsymbol{r}(x_1)-\boldsymbol{r}(x_2)|^2\rangle$, and clouds the correct interpretation that R_G^2 gives the distribution of the monomers about the centre of mass. It is desirable to disentangle the radius of gyration R_G^2 from the end-to-end distance. At the level of the distribution function this can be achieved by including a global constraint (using the Dirac delta function) [1, 4]:

$$P(R_G^2) = \int \delta\left(R_G^2 - \sum_{kl} g_{kl}\boldsymbol{s}_k\cdot\boldsymbol{s}_l\right)P\{\boldsymbol{s}\}\,\mathrm{d}\{\boldsymbol{s}\} \tag{1.5}$$

where $\boldsymbol{s}_i \equiv \boldsymbol{r}_i - \boldsymbol{r}_{i-1}$ are bond vectors linking the monomers located at $\boldsymbol{r}_i$ and $\boldsymbol{r}_{i-1}$; g_{kl} is a matrix to be determined. (For the continuous case see, e.g., [5]). An analogous expression for the probability distribution of the end-to-end distance R_E^2 is $P(R_E^2) = \int \delta(\boldsymbol{R}_E - \boldsymbol{r}_n - \boldsymbol{r}_0)P\{\boldsymbol{s}\}\,\mathrm{d}\{\boldsymbol{s}\}$, where $\boldsymbol{r}_0$ and $\boldsymbol{r}_n$ are, respectively, the position of the first and of the last monomer. In this treatment the radius of gyration and the end-to-end distance are regarded as more or less independent quantities.

In this paper we propose a new approach for the calculation of the radius of gyration that treats R_G as a fundamental object, and is inspired by studies of membranes and surfaces. In their study of lamellar fluid membranes Golubović and Lubensky [6] control fluctuations in the total surface area A by (a) introducing into the partition function a global constraint:

$$\delta\left(A - \int \mathrm{d}^2\xi\, g^{1/2}(\boldsymbol{\xi})\right) \qquad g = \det g_{ij} \tag{1.6}$$

where $g_{ij}(\boldsymbol{\xi})$ is the metric tensor, or (b) adding a surface tension term

$$H_A = \sigma\int \mathrm{d}^2\xi\, g^{1/2}(\boldsymbol{\xi}) \tag{1.7}$$

to the bending Hamiltonian. The latter case allows for fluctuations in the total surface area and corresponds physically to a situation where exchange of molecules takes place between the fluid membrane and a reservoir consisting of an ensemble of many surfaces (or molecules), the chemical potential of the reservoir being $-\sigma/a^2$, where a^2 is the fixed area occupied by each molecule [6]. The form (1.7) has been used to describe configurations of a crystal–vapour interface at high temperatures. In that work the Monge representation of g_{ij} is used together with a further approximation to reduce the reparametrization invariant form (1.7) to a more familiar gradient of the height of the interface, $(\sigma/2)\int \mathrm{d}^2x|\boldsymbol{\nabla}h|^2$ [7].

In order to apply equation (1.7) to polymers we note that Brownian motion (fractal dimension two) can be characterized by an 'area' [8]. The fluctuations in this area can be controlled by adding a term $\mu\,\mathrm{tr}\,\mathcal{T}$ to the original Hamiltonian $\mathcal{H}_0$ describing the connectivity of the chain. Here $\mathcal{T}$ is the inertia (or shape) tensor [9] whose eigenvalues give the size,

$$R_G^2 = \langle\mathrm{tr}\,\mathcal{T}\rangle. \tag{1.8}$$

Consequently the partition function for a Gaussian chain consisting of n links is [10]

$$Z_n(\mu) = \int D[\boldsymbol{r}]\exp(-\mu\,\mathrm{tr}\,\mathcal{T} - H_0) \tag{1.9}$$

where $D[\boldsymbol{r}] = \prod_{\alpha=1}^{d}\prod_{i=1}^{n}\mathrm{d}r_{i\alpha}$, $r_{i\alpha}$ being the αth component of the position vector of the ith monomer. The preceding discussion suggests that $Z_n(\mu)$ is the canonical partition function for a Gaussian chain. Use in $Z_n(\mu)$ of a geometric invariant, $\mathrm{tr}\,\mathcal{T}$, representing the size,

is motivated by the reparametrization invariance of the form in equation (1.7). As recently noted [11], there is no direct relationship (in the literature) between the Hamiltonian of a Gaussian polymer chain and the canonical partition function. In [11] a canonical partition function for a different model, the freely jointed chain, was constructed.

The distribution function $\rho_{\rm col}\{\mathbf{r}_i\} \propto \exp[-(3/2\tilde{b}_{\rm col}^2)\sum_{i=1}^{n}(\mathbf{r}_i - \bar{\mathbf{r}})^2]$, where $\bar{\mathbf{r}}$ is the centre of mass, has been shown in the context of 'constraint-induced localization' [12] to encompass the extended and compact phases of a Gaussian chain. Since the distribution function $\rho_{\rm col}\{\mathbf{r}_i\}$ is equivalent [10] to the form $\exp(-\mu\,\mathrm{tr}\,\mathcal{T})$, the extended and compact phases are expected to occur, and to depend on the 'chemical potential' μ; this will be shown below to be indeed the case.

To study the size of an n-link polymer chain, we will evaluate the function

$$C_n(\boldsymbol{k},\mu) = \langle \exp(-\mu\,\mathrm{tr}\,\mathcal{T} + \mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{r}_u - \boldsymbol{r}_v])\rangle \tag{1.10}$$

in which the radius of gyration $R_{\rm G}^2$ and the end-to-end distance $R_{\rm E}^2$ (obtainable from the $\boldsymbol{k}$ term) are placed on an equal footing, in contrast to usual practice (equations (1.2)–(1.4)). Thus, from equation (1.10), we obtain

$$R_{\rm G}^2 = -\frac{\partial}{\partial\mu}\ln C_n(0,\mu)|_{\mu=0} \tag{1.11}$$

and

$$R_{\rm E}^2 = -\nabla_k^2 C_n(\boldsymbol{k},0)|_{\boldsymbol{k}=0} \tag{1.12}$$

with $u = n$, $v = 1$.

The aim of this paper is to calculate the size ($R_{\rm G}^2$ and $R_{\rm E}^2$) of a polymer chain, using a discrete model (described in section 2) and equations (1.9)–(1.12). We make extensive use of the hypergeometric function ${}_2F_1(n,-m;c;-z^2)$, where n and m are integers. Here $z^2 = \mu/(4n\gamma)$, where γ is the coefficient in $\mathcal{H}_0$. The radius of gyration for a Gaussian chain is calculated in section 3, where we recover known results in the limit $n \to \infty$ of ${}_2F_1(n,-m;c;-z^2)$, including the one obtained in [13] in connection with the shape of a Gaussian chain. The excluded volume problem is taken up in section 4. Discretizing the Fourier transform of the interaction $\iint \mathrm{d}s\,\mathrm{d}s'\,\delta^d[\boldsymbol{r}(s)-\boldsymbol{r}(s')]$, due to Edwards [14], to a form that is similar to the right-hand side of equation (1.1), we obtain the dimensionally regularized parts of $R_{\rm G}^2$ and of $R_{\rm E}^2$ to first order in $\epsilon = 4 - d$, where d is the dimension of space; our results agree with the earlier works of des Cloizeaux [8] and Duplantier [15] which were based on Edwards' continuous model [14].

The function $C_n(0,\mu)$ (equivalently, the partition function $Z_n(\mu)$) can also be used to determine the asphericity parameter [9, 13] of a Gaussian polymer chain. This will be pursued elsewhere.

2. The model

Consider an ideal, Gaussian chain consisting of n identical links (or monomers) in a d-dimensional space. The monomers are labelled by an index $i (1 \leqslant i \leqslant n)$, and the position vector of the ith monomer is $\boldsymbol{r}_i = (r_{i1}, r_{i2}, \ldots, r_{id})$. For harmonic interactions between nearest neighbours with mean separation ℓ, we write the Hamiltonian of the system as

$$\mathcal{H}_0 = \gamma\sum_{i=1}^{n}(\boldsymbol{r}_i - \boldsymbol{r}_{i-1})^2 \qquad \gamma = 1/(2\ell)^2. \tag{2.1}$$

The properties of the chain can be determined from the inertia tensor $\mathcal{T}$ [9]

$$\mathcal{T}_{\alpha\beta} = \frac{1}{2n^2}\sum_{i,j=1}^{n}(r_{i\alpha}-r_{j\alpha})(r_{i\beta}-r_{j\beta}). \tag{2.2}$$

By definition the radius of gyration is

$$R_{\mathrm{G}}^2 = \langle\overline{(\boldsymbol{r}-\bar{\mathbf{r}})^2}\rangle \tag{2.3}$$

where $\bar{\mathbf{r}} = (1/n)\sum_{i=1}^{n}\boldsymbol{r}_i$ is the centre of mass of the chain and the brackets $\langle\ \rangle$ denote an ensemble average. It can easily be shown that the forms (1.8) and (2.3) are equivalent.

The excluded volume interaction will be modelled according to Edwards [14] as

$$\mathcal{H}_{\mathrm{int}} = \frac{b}{2}\int_0^S \mathrm{d}s\int_0^S \mathrm{d}s'\,\delta^d[\boldsymbol{r}(s)-\boldsymbol{r}(s')] \tag{2.4}$$

where S is the area of the Brownian chain [8]. Implicit in the double integral is the constraint that $|s-s'|$ is larger than some minimum length s_0 [8]. The model is valid for $b>0$, i.e. for binary repulsion between links. It is convenient to take the Fourier transform

$$\delta^d[\boldsymbol{r}(s)-\boldsymbol{r}(s')] = \int_{\boldsymbol{k}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{r}(s)-\boldsymbol{r}(s')]} \tag{2.5}$$

where $\int_{\boldsymbol{k}} \equiv (1/(2\pi)^d)\int \mathrm{d}^dk$, and s, s' are continuous variables along the chain. Upon descritizing the path $\boldsymbol{r}(s)\to\boldsymbol{r}_u, \boldsymbol{r}(s')\to\boldsymbol{r}_v$, the exponent in equation (2.5) becomes $\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{r}_u-\boldsymbol{r}_v]$, which is the form appearing in equation (1.1). In a perturbative expansion involving powers of the excluded volume interaction, we will obtain a term of the form $\exp(-\mu\,\mathrm{tr}\,\mathcal{T}-\mathcal{H}_0+\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{r}_u-\boldsymbol{r}_v])$ (see equation (4.5) below), the integral of which can be easily obtained since $\mathrm{tr}\,\mathcal{T}$ and $\mathcal{H}_0$ are quadratic in the coordinates. We then evaluate the integral $\iint_{|u-v|>n_0}\mathrm{d}u\,\mathrm{d}v$, where the cut off corresponds to the one employed in equation (2.4) to control divergencies of the continuous theory. Alternatively, one could take the *sum* over u and v, as is done in [16], in which the cut off plays no role. Our strategy here of mixing up (so to speak) the continuous and discrete variables, viz, replacing $\boldsymbol{r}(s)$ by $\boldsymbol{r}_u$ (s continuous; u discrete), and integrating over u, is akin to the scheme devised by Fixman [1], where discrete variables were replaced by continuous ones for the purpose of diagonalizing a matrix. This led to an infinite set of eigenvalues and eigenfunctions, from which the proper set was extracted at the end by noting that some of the elements in this infinite set were redundant [1]. Here we show that the essential features of the problem, viz, the dimensionally regularized form for the size, as well as the cut-off dependence, are preserved when we discretize the continuous path $\boldsymbol{r}(s)$ for convenience.

3. Size of a Gaussian chain

3.1. The function $C_n(0,\mu)$

In this section we calculate the radius of gyration of a Gaussian chain using equation (1.11) which involves $C_n(0,\mu)$ (equivalently, $Z_n(\mu)$ in equation (1.9)). The exponent $\mu\,\mathrm{tr}\,\mathcal{T}+\mathcal{H}_0$ in equation (1.9) is a quadratic form $\mathbf{r}^{\mathrm{T}}\mathbf{M}\mathbf{r}$, where the matrix $\mathbf{M}$ is given by

$$M_{ij}(\mu) = \begin{cases} 2\gamma+a-b & i=j=1,2,\ldots,n-1 \\ \gamma+a-b & i=j=n \\ -(\gamma+b) & |i-j|=1 \\ -b & |i-j|>1 \end{cases} \tag{3.1}$$

where $a=\mu/n$ and $b=\mu/n^2$.

In order to eliminate the zero eigenvalue (corresponding to translational motion of the centre of mass) from the determinant which results when we carry out the Gaussian integration in equation (1.9), we keep one tail end of the chain fixed at the origin ($\boldsymbol{r}_0 = 0$). Hence the different factors 2γ and γ in the first and second line, respectively, in equation (3.1). The result is

$$C_n(0,\mu) = \left[\frac{\det \mathbf{M}(\mu)}{\det \mathbf{M}(0)}\right]^{-d/2}. \tag{3.2}$$

By equation (A18) in the appendix, $C_n(0,\mu)$ can be written as

$$C_n(0,\mu) = [{}_2F_1(n+1,-n+1;\tfrac{3}{2};-z^2)]^{-d/2} \qquad z^2 = \mu/(4n\gamma) \tag{3.3}$$

where

$${}_2F_1(n+1,-n+1;\tfrac{3}{2};-z^2) = \frac{1}{4nz\sqrt{1+z^2}}[(\sqrt{1+z^2}+z)^{2n} - (\sqrt{1+z^2}-z)^{2n}] \tag{3.4}$$

by equation (A15). Thus the function $C_n(0,\mu)$ is expressed in terms of a hypergeometric function. This is our key result. Quantities derived from $C_n(0,\mu)$, such as R_G^2 in equation (1.11), and the thermodynamic limit ($n \to \infty, \ell \to 0$, with $n\ell^2$ fixed), which corresponds to $z \to 0$, will depend on the properties of the function ${}_2F_1(n+1,-n+1;\frac{3}{2};-z^2)$. This function is related [17, 26] to the Jacobi polynomial $P_{n-1}^{(\alpha,\beta)}(w)$, with $\alpha = \beta = 1/2$ and $w = 1 + 2z^2$. The importance of orthogonal polynomials was recently highlighted in the context of a 'quasi-exactly solvable model' [18]. As shown in that work, the solution ψ of the Schrödinger equation, $H\psi = E\psi$, for a particular H, is a generating function for an orthogonal set $P_n(E)$ obeying a three-term recursion relation. In the same spirit, and in view of the intimate connection [14, 19] between the polymer problem and quantum mechanics (and field theory), here we express the partition function $C_n(0,\mu)$ in terms of the (orthogonal) Jacobi polynomial whose argument, $w = (\gamma + \mu/4n)/\gamma$, is a dimensionless ratio of the coefficients appearing in the Hamiltonian of equation (1.9).

We emphasize that the result in equation (3.3) is an *exact* expression for *finite* n, in contrast to the evaluation of $P(R_G^2)$ in equation (1.5), which can only be done approximately, using, for example, the saddle-point method. This is the approximation used in [1, 4]. Diehl and Eisenriegler [13] studied the function $C_n(0,\mu)$ in connection with the asphericity of a Gaussian chain. Their method involved diagonalization of a quadratic form; they obtain a closed form expression for $C_n(0,\mu)$ only in the limit $n \to \infty$. We recover their result as follows. Since $z \to 0$ corresponds to the thermodynamic limit, we expand the right-hand side of equation (3.4) up to first order in $z(= \sqrt{\mu L/n^2})$, where $L = n\ell^2$ is fixed. We note that $(1 \pm z)^{2n} \to \mathrm{e}^{\pm 2\sqrt{\mu L}}$ as $n \to \infty$. Inserting this into equation (3.3), we find

$$C_n(0,\mu) = \left(\frac{\sinh(2\sqrt{\mu L})}{2\sqrt{\mu L}}\right)^{-d/2} \tag{3.5}$$

in agreement with [13]. The form in equation (3.5) can also be obtained from the hypergeometric series, equation (A23), by taking the limit $n \to \infty$, with $n\ell^2$ fixed (i.e. $z \ll 1$), without use of the explicit form (3.4) for the hypergeometric function. It is the special values of the arguments $a = n+1$, $b = -n+1$, and $c = 3/2$ that give rise to the form (3.5).

The condition $z \ll 1$ gives the relative importance of the two terms $\mu \,\mathrm{tr}\,\mathcal{T}$ and $\mathcal{H}_0$ in the exponent of equation (1.9), since $z^2 \propto \mu/\gamma$. Thus, if $z \ll 1$, the properties of the chain are determined primarily by the connectivity term $\mathcal{H}_0$. It would be instructive to give another interpretation of the variable z. Setting $\mu = \alpha/\ell_c^2$, where ℓ_c is a microscopic length associated with the centre of mass, and α is dimensionless, we can express z as a ratio

$$z = \ell_{\mathrm{eff}}/\xi_c \tag{3.6}$$

where $\ell_{\rm eff}(=\alpha^{1/2}\ell)$ is the effective step length along the chain, and $\xi_{\rm c}(=n^{1/2}\ell_{\rm c})$ is the correlation length associated with the centre of mass. Therefore one finds, approximately, $0 < z < 1$. Clearly $\xi_{\rm c} \gg \ell_{\rm eff}$ describes an 'extended' object, i.e. a Gaussian chain (or random walk). The case $z \approx 1$ corresponds to a 'compact' object, as we will show in the next subsection.

3.2. Radius of gyration

The radius of gyration for a Gaussian chain is obtained from equations (1.11) and (3.3). We obtain

$$R_{\rm G}^2 = \frac{d}{3}\frac{L}{n^2}(n+1)(n-1) \tag{3.7}$$

where $L = n\ell^2$. Here we have used equation (A14) in the appendix, and

$${}_2F_1(a, b; c; 0) = 1 \tag{3.8}$$

which is obvious, by the hypergeometric series (A23) or equations (A13) and (A15). All the moments of $R_{\rm G}^2$ can be obtained by differentiating repeatedly with respect to μ. In particular, the fluctuations are given by

$$\Delta R_{\rm G}^2(\mu) = \langle (R_{\rm G}^2)^2\rangle - \langle R_{\rm G}^2\rangle^2 = \frac{\partial}{\partial\mu} R_{\rm G}^2(\mu) \tag{3.9}$$

according to the linear response theorem, which gives

$$\Delta R_{\rm G}^2(0) = \frac{2d}{45}\frac{L^2}{n^4}(n^2-1)(7+2n^2) \tag{3.10}$$

or

$$\frac{\Delta R_{\rm G}^2}{(R_{\rm G}^2)^2} = \frac{4}{5d}\left[1 + \frac{9}{2(n^2-1)}\right] \tag{3.11}$$

for the relative fluctuations in the limit $z \to 0$. It is clear from equation (3.11) that the relative fluctuations do not vanish in the limit of a very long chain ($n \to \infty$); they do vanish in a high-dimensional space ($d \to \infty$), in accord with a recent Monte Carlo study [20].

For finite $\mu > 0$ equations (1.11) and (3.3) give

$$R_{\rm G}^2(\mu) = R_{\rm G}^2(0)\frac{{}_2F_1(n+2, -n+2; \frac{5}{2}; -z^2)}{{}_2F_1(n+1, -n+1; \frac{3}{2}; -z^2)} \tag{3.12}$$

where $R_{\rm G}^2(0)$ is given by equation (3.7). The ratio in equation (3.12) is a decreasing function of z^2, which indicates that the limit $z \to 1$ corresponds to the collapsed phase of a polymer chain. To show this we note that (equation (A25))

$${}_2F_1(n+1, -n+1; \tfrac{3}{2}; -z^2)|_{z=1} = \frac{1}{4\sqrt{2}n}[(\sqrt{2}+1)^{2n} - (\sqrt{2}-1)^{2n}] \tag{3.13}$$

and

$${}_2F_1(n+2, -n+2; \tfrac{5}{2}; -z^2)|_{z=1} = \frac{3}{16(n^2-1)}\left[(\sqrt{2}+1)^{2n}\left(1 - \frac{3}{n\sqrt{8}}\right)\right.$$
$$\left. +(\sqrt{2}-1)^{2n}\left(1 + \frac{3}{n\sqrt{8}}\right)\right] \tag{3.14}$$

which was obtained by differentiating both sides of equation (3.4), and setting $z = 1$. Substituting equations (3.13) and (3.14) into (3.12), we get

$$\frac{R_G^2(\mu)}{R_G^2(0)} = \begin{cases} 1 & z \ll 1 \\ 3/(n\sqrt{8}) & z = 1, n \to \infty. \end{cases} \tag{3.15}$$

This is in accord with the free energy estimates of [12], which suggested that $R_G^2 \sim n$ for the extended conformation ($z \ll 1$) and $R_G^2 \sim \mathcal{O}(1)$ for the collapsed conformation ($z \approx 1$).

4. Polymer chain with excluded volume

4.1. Radius of gyration

In this section we calculate the radius of gyration of a polymer chain with excluded volume interactions. A long, flexible polymer chain in a good solvent, with a short-ranged interaction between links, is described by Edwards' model [14]

$$\mathcal{H}_{\rm int} = b \int_0^L \int_{|s-s'|>s_0}^L \mathrm{d}s\, \mathrm{d}s'\, \delta^d[\boldsymbol{r}(s) - \boldsymbol{r}(s')] \tag{4.1}$$

where we include the cut off implicit in equation (2.4), and denote by L the contour size of the chain. In the presence of interactions the function $C_n(0, \mu)$ of equation (1.10) becomes

$$C_n(0, \mu) = \langle \mathrm{e}^{-\mu\, \mathrm{tr}\, \mathcal{T}} \rangle_{\mathcal{H}} \equiv \mathcal{N}^{-1} \int D[\boldsymbol{r}]\, \mathrm{e}^{-\mu\, \mathrm{tr}\, \mathcal{T}} \tag{4.2}$$

where $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\rm int}$, and $\mathcal{N} = \int D[\boldsymbol{r}]\, \mathrm{e}^{-\mathcal{H}}$.

Expanding equation (4.2) to first order in $\mathcal{H}_{\rm int}$, we get

$$C_n(0, \mu) = \langle \mathrm{e}^{-\mu\, \mathrm{tr}\, \mathcal{T}} \rangle_0 - \langle \mathrm{e}^{-\mu\, \mathrm{tr}\, \mathcal{T}} \mathcal{H}_{\rm int} \rangle_0 + \langle \mathrm{e}^{-\mu\, \mathrm{tr}\, \mathcal{T}} \rangle_0 \langle \mathcal{H}_{\rm int} \rangle_0 \tag{4.3}$$

where $\langle\rangle_0$ denotes an average with respect to the Gaussian Hamiltonian $\mathcal{H}_0$ given by equation (2.1). Using the Fourier transform of the δ-function (equation (2.5)), the second term on the right-hand side of equation (4.3) becomes

$$\langle \mathrm{e}^{-\mu\, \mathrm{tr}\, \mathcal{T}} \mathcal{H}_{\rm int} \rangle_0 = b \mathcal{N}_0^{-1} \int_0^L \int_{|s-s'|>s_0}^L \mathrm{d}s\, \mathrm{d}s' \int_{\boldsymbol{k}} \int \mathrm{e}^{-\mathcal{H}_\mu + \mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{r}(s) - \boldsymbol{r}(s')]} \tag{4.4}$$

where $\mathcal{H}_\mu = \mu\, \mathrm{tr}\, \mathcal{T} + \mathcal{H}_0$, and $\mathcal{N}_0 = \int D[\boldsymbol{r}]\, \mathrm{e}^{-\mathcal{H}_0}$.

In order to evaluate the integral in equation (4.4) by the matrix methods developed here we use a discrete representation of the path, as explained in section 2: $\boldsymbol{r}(s) \to \boldsymbol{r}_u$, $\boldsymbol{r}(s') \to \boldsymbol{r}_v$, and set $s = u\ell^2$, $s' = v\ell^2$. The last integral in equation (4.4) (including the normalization factor $\mathcal{N}_0^{-1}$) can then be written as

$$I(k) = \mathcal{N}_0^{-1} \int D[\boldsymbol{r}] \exp(-\mu\, \mathrm{tr}\, \mathcal{T} - \mathcal{H}_0 + \mathrm{i}\boldsymbol{k} \cdot [\boldsymbol{r}_u - \boldsymbol{r}_v]). \tag{4.5}$$

We note that $\mu\, \mathrm{tr}\, \mathcal{T} = a \sum_{i\alpha} r_{i\alpha}^2 - \beta \sum_\alpha \sum_{ij} r_{i\alpha} r_{j\alpha}$, with $a = \mu/n$ and $\beta = \mu/n^2$. Substituting this form into equation (4.5) gives an exponential factor $\exp[\beta(\sum_i r_{i\alpha})^2]$, which can be conveniently written as

$$\exp\left[+ \beta \left(\sum_i r_{i\alpha} \right)^2 \right] = (4\pi\beta)^{-1/2} \int_{-\infty}^{\infty} \mathrm{d}\psi \exp\left(- \frac{1}{4\beta} \psi^2 - \psi \sum_i r_{i\alpha} \right). \tag{4.6}$$

We carry out the integral in equation (4.5), using

$$\int D\boldsymbol{X}\, \mathrm{e}^{-\boldsymbol{X}^{\mathrm{T}} \mathbf{A} \boldsymbol{X} + \mathbf{V}^{\mathrm{T}} \boldsymbol{X}} = \pi^{n/2} (\det \mathbf{A})^{-1/2} \exp(\tfrac{1}{4} \mathbf{V}^{\mathrm{T}} \mathbf{A}^{-1} \mathbf{V}) \tag{4.7}$$

where $\mathbf{A}$ is an $n \times n$ non-singular matrix, and $\boldsymbol{X}$ is an n-component column vector. The result is

$$I(k) = (4\pi\beta)^{-d/2}\left(\frac{\det \mathbf{A}(\mu)}{\det \mathbf{A}(0)}\right)^{-d/2}\int [\mathrm{d}\psi]\,\mathrm{e}^{-F(\psi,k)}. \tag{4.8}$$

The function F is given by

$$F(\psi,k) = \frac{1}{4\beta}\left(1-\beta\sum_{ij}A^{-1}_{ij}\right)\sum_{\alpha}\psi^2_{\alpha} + \frac{1}{4}\boldsymbol{k}^2 g_{uv} + \frac{\mathrm{i}}{2}t_{uv}\boldsymbol{k}\cdot\boldsymbol{\psi} \tag{4.9}$$

where

$$g_{uv}(\mu) = A^{-1}_{uu} + A^{-1}_{vv} - 2A^{-1}_{uv} \tag{4.10}$$

$$t_{uv}(\mu) = \sum_{i=1}^{n}(A^{-1}_{iu} - A^{-1}_{iv}) \tag{4.11}$$

and $\mathbf{A}(\mu)$ is a tridiagonal (or Töplitz) matrix:

$$\mathbf{A}_{ij}(\mu) = \begin{cases} 2\gamma + a & i = j < n \\ -\gamma & |i-j| = 1 \\ \gamma + a & i = j = n \\ 0 & \text{otherwise.} \end{cases} \tag{4.12}$$

Integration over ψ in equation (4.8) leads to

$$I(k) = I(0)\exp(-\boldsymbol{k}^2 G_{uv}) \tag{4.13}$$

where

$$G_{uv}(\mu) = \frac{1}{4}g_{uv} + \frac{t^2_{uv}}{16c} \tag{4.14}$$

c is the coefficient of $\sum_{\alpha}\psi^2_{\alpha}$ in equation (4.9), and

$$I(0) = \left[\frac{\det \mathbf{A}(\mu)}{\det \mathbf{A}(0)}\left(1-\beta\sum_{ij}A^{-1}_{ij}\right)\right]^{-d/2}. \tag{4.15}$$

The right-hand side of equation (4.15) is another form for $C_n(0,\mu)$, given by equation (3.3). Since $\det \mathbf{A}$ is given by equation (A22), we immediately obtain an expression for c:

$$c \equiv \frac{1}{4\beta}\left(1-\beta\sum_{ij}A^{-1}_{ij}\right) = \frac{1}{4\beta}\frac{{}_2F_1(n+1,-n+1;\frac{3}{2};-z^2)}{{}_2F_1(n+1,-n;\frac{1}{2};-z^2)}. \tag{4.16}$$

Returning to the perturbation expansion of equation (4.3), we note that $\langle\mathcal{H}_{\mathrm{int}}\rangle_0$ there can be obtained from the second term by setting $\mu = 0$. Equation (4.3) can therefore be written as

$$C_n(0,\mu) = Z_0 - b\ell^4\int_{\boldsymbol{k}}\int_{|u-v|>n_0}^{n}\mathrm{d}u\,\mathrm{d}v\,I(k) + Z_0 b\ell^4\int_{\boldsymbol{k}}\int_{|u-v|>n_0}^{n}\mathrm{d}u\,\mathrm{d}v\,I(k)||_{\mu=0} \tag{4.17}$$

where $Z_0 \equiv \langle\,\mathrm{e}^{-\mu\,\mathrm{tr}\,\mathcal{T}}\rangle_0$ and $I(k)$ is given by equation (4.13). The radius of gyration is obtained by differentiating equation (4.17) with respect to μ and setting $\mu = 0$:

$$R^2_{\mathrm{G}} = R^2_{\mathrm{G}^0} - b\ell^4\int_{\boldsymbol{k}}\boldsymbol{k}^2\int_{|u-v|>n_0}^{n}\mathrm{d}u\,\mathrm{d}v\,\mathrm{e}^{-\boldsymbol{k}^2 G_{uv}}\frac{\mathrm{d}}{\mathrm{d}\mu}G_{uv}\bigg|_{\mu=0} \tag{4.18}$$

where $R^2_{\mathrm{G}^0}$ is the size of a Gaussian chain (i.e. one without excluded volume interactions). It is, therefore, only necessary to expand G_{uv} to first order in $\mu(\propto z^2)$.

Using the standard formula

$$\mathbf{A}^{-1} = \frac{\text{adj}\,\mathbf{A}}{|A|} \tag{4.19}$$

(adj the adjoint) for the inverse, we obtain

$$A^{-1}_{uv} = \frac{1}{\det \mathbf{A}} D_{u-1} A_{n-v} \gamma^{v-u} \qquad u \leqslant v \tag{4.20}$$

for the matrix A_{uv} of equation (4.12). D_k is the determinant of the $k \times k$ matrix given by equation (A3), and the determinant A_{n-v} is obtained by deleting rows and columns 1 to v from the original $n \times n$ matrix $\mathbf{A}$ of equation (4.12). The indices u and v in equation (4.20) are interchanged for the case $u > v$.

We can express A^{-1}_{uv} in terms of hypergeometric functions by noting from equations (A17) and (A22) that $D_{u-1} = u\gamma^{u-1}\,{}_2F_1(-u+1, u+1; \frac{3}{2}; -z^2)$ and $A_k = \gamma^k\,{}_2F_1(-k, k+1; \frac{1}{2}; -z^2)$. Thus, for $u \leqslant v$, equation (4.20) becomes

$$A^{-1}_{uv} = \frac{u}{\gamma F_n}\,{}_2F_1(-u+1, u+1; \tfrac{3}{2}; -z^2)\,{}_2F_1(-n+v, n-v+1; \tfrac{1}{2}; -z^2) \tag{4.21}$$

where $F_n \equiv {}_2F_1(-n, n+1; \frac{1}{2}; -z^2)$. We note that the inverse A^{-1}_{uv} decomposes into a product of two hypergeometric functions with different arguments u and v. The indices u and v in equation (4.21) are interchanged for the case $u > v$. Thus the inverse, given by equation (4.21), is a symmetric matrix. Expanding the right-hand side of equation (4.21) to $\mathcal{O}(z^2)$, and substituting into equation (4.10), we obtain

$$g_{uv}(\mu) = \frac{1}{\gamma}\left[|u-v| - \frac{4}{3}z^2(u-v)^2(3n - 2w_> - w_<)\right] \tag{4.22}$$

where factorization of the extra $(u-v)$ in the z^2 term was achieved by neglecting terms of order unity, and $w_>(w_<)$ represents the larger(smaller) of the pair (u, v). Similarly,

$$t_{uv}(0) = \frac{1}{2\gamma}(u-v)[2n+1-u-v] \tag{4.23}$$

which follows after some algebra, and, from equation (4.16),

$$c = \frac{n}{16z^2\gamma}\left[1 - \frac{2}{3}z^2(n+1)(2n+1)\right] \qquad z^2 = \mu/(4n\gamma) \tag{4.24}$$

to first order in z^2. As in the calculation of g_{uv}, we will neglect the number 1 in the square bracket of equation (4.23), since it is of little consequence. Combination of equations (4.14) and (4.22)–(4.24) yields

$$\left.\frac{\mathrm{d}}{\mathrm{d}\mu}G_{uv}\right|_{\mu=0} = -\frac{1}{12n\gamma^2}(u-v)^2(3n - 2w_> - w_<) + \frac{1}{16n^2\gamma^2}(u-v)^2[2n-u-v]^2. \tag{4.25}$$

Since $G_{uv}(\mu = 0) = (1/4\gamma)|u-v|$, the k-integral in equation (4.18) evaluates to [21]

$$\frac{1}{(2\pi)^d}\int \mathrm{d}^d k\, \boldsymbol{k}^2 \exp\left(-\frac{\boldsymbol{k}^2}{4\gamma}|u-v|\right) = \frac{\mathrm{d}}{2}\frac{\pi^{d/2}}{(2\pi)^d}\ell^{-2-d}|u-v|^{-1-d/2} \tag{4.26}$$

so that the size, given by equation (4.18), becomes

$$R^2_{\mathrm{G}} = R^2_{\mathrm{G}^0} - \frac{d}{2}b\frac{\pi^{d/2}}{(2\pi)^d}\ell^{2-d}(I_1 + I_2) \tag{4.27}$$

where

$$I_1 = -\frac{4L^2}{3n^3}\int_0^n \int_{|u-v|>n_0}^n \mathrm{d}u\,\mathrm{d}v\,|u-v|^{-1-d/2}(u-v)^2(3n-2w_>-w_<) \tag{4.28}$$

$$I_2 = \frac{L^2}{n^4}\int_0^n \int_{|u-v|>n_0}^n \mathrm{d}u\,\mathrm{d}v\,|u-v|^{-1-d/2}(u-v)^2(2n-u-v)^2. \tag{4.29}$$

The integrals I_1 and I_2 can be written in the form

$$T = m\int_0^n \int_{|u-v|>n_0}^n \mathrm{d}u\,\mathrm{d}v\,|u-v|^{\alpha}v^{\beta}. \tag{4.30}$$

Making a change of variables $x = u - v$, $y = v$, and taking the cut-off into account, we have $T = 2m\int_{n_0}^n \mathrm{d}x\,x^{\alpha}\int_0^n \mathrm{d}y\,y^{\beta}$. In this form T can be evaluated using the beta function $B(\mu,\nu)$ defined by [21]

$$\int_0^u (u-x)^{\mu-1}x^{\nu-1}\,\mathrm{d}x = u^{\mu+\nu-1}B(\mu,\nu) \qquad \mathrm{Re}\,\mu > 0, \mathrm{Re}\,\nu > 0. \tag{4.31}$$

It is convenient to split up the integral as $\int_{n_0}^n \to \int_0^n - \int_0^{n_0}$, which leads to

$$T = \frac{2m}{\beta+1}n^{\alpha+\beta+2}B(\alpha+1,\beta+2) - \frac{2m}{\beta+1}\int_0^{n_0}\mathrm{d}x\,x^{\alpha}(n-x)^{\beta+1}. \tag{4.32}$$

Use of the properties of the beta function [21] simplifies the sums of the form T to

$$I_1 = -\frac{8}{3}L^2n^{d_1}\frac{d_5}{d_2d_3d_4} + \Delta_1(n_0) \tag{4.33}$$

$$I_2 = 2L^2n^{d_1}\frac{1}{d_2d_3}\left(1+\frac{2}{d_4d_5}\right) + \Delta_2(n_0) \tag{4.34}$$

where $d_k = k - d/2$ and Δ_1, Δ_2 are cut-off dependent terms.

Substituting equations (4.33) and (4.34) into (4.27), and redefining the parameters $\ell^2 \to \ell^2/2$, $b \to b/2$, we obtain the dimensionally regularized part of R_{G}^2:

$$R_{\mathrm{G}}^2 = \frac{Ld}{6}\left[1+\frac{z}{(2-d/2)(3-d/2)}\left(1+\frac{4}{4-d/2}-\frac{6}{(4-d/2)(5-d/2)}\right)\right] \tag{4.35}$$

where $z = bL^{2-d/2}(2\pi)^{-d/2}$, and the sum of the cut-off dependent terms is

$$\Delta \equiv \Delta_1 + \Delta_2 = Ln^{1-d/2}\left[\frac{14}{3}\frac{1}{2-d/2}x_0^{2-d/2} - \frac{26}{3}\frac{1}{3-d/2}x_0^{3-d/2} + \mathcal{O}(x_0^{4-d/2})\right]$$
$$x_0 \equiv n_0/n. \tag{4.36}$$

The ϵ-expansion ($\epsilon = 4 - d$) of R_{G}^2 follows:

$$R_{\mathrm{G}}^2/R_{\mathrm{G}^0}^2 = 1 + \frac{2}{3}\left(1-\frac{13}{24}\epsilon\right)z \tag{4.37}$$

in agreement with [8, 15]. In [15] Duplantier calculates partition functions, which exhibit a divergence of the form $x_0^{1-d/2}$. The radius of gyration is given by a ratio of these partition functions, and this divergence cancels out. This is due to factorization of $\exp[(L/n_0)F]$ in the partition function, where F is the local free energy associated with the short distance divergences [8, 15]. Here too the divergence cancels out. We calculate the physical quantity, R_{G}^2, directly, as a derivative of the function $\langle\exp(-\mu\,\mathrm{tr}\,\mathcal{T})\rangle$ (equation (4.2)), and find in equations (4.35) and (4.36) that the radius of gyration has no 'ultra-violet' divergence in the region $d < 4$ where the excluded volume interaction is relevant. This cancellation of divergences is closely tied with the nature of the perturbation expansion in equation (4.3).

4.2. End-to-end distance

The ratio R_G^2/R_E^2 is universal [22]. We therefore have to compute R_E^2 to complete our analysis. Consider, therefore, the (discretized) Fourier transform $\exp(\mathrm{i}\boldsymbol{q}\cdot[\boldsymbol{x}_u-\boldsymbol{x}_v])$ and expand it to first order in powers of $\mathcal{H}_{\rm int}$ as in equation (4.3), obtaining

$$\langle \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot[\boldsymbol{x}_u-\boldsymbol{x}_v]}\rangle = \langle \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot[\boldsymbol{x}_u-\boldsymbol{x}_v]}\rangle_0 - b\ell^4\int_{\boldsymbol{k}}\int \mathrm{d}r\,\mathrm{d}p\,\langle \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot[\boldsymbol{x}_u-\boldsymbol{x}_v]+\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{x}_r-\boldsymbol{x}_p]}\rangle_0$$
$$+b\ell^4\langle \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot[\boldsymbol{x}_u-\boldsymbol{x}_v]}\rangle_0\int_{\boldsymbol{k}}\int \mathrm{d}r\,\mathrm{d}p\langle \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{x}_r-\boldsymbol{x}_p]}\rangle_0. \tag{4.38}$$

It is instructive to look upon the averages in equation (4.38) as special cases of

$$C_n(\boldsymbol{k},\boldsymbol{q};\mu)\equiv\langle\exp(-\mu\,\mathrm{tr}\,\mathcal{T}+\mathrm{i}\boldsymbol{k}\cdot[\boldsymbol{x}_r-\boldsymbol{x}_p]+\mathrm{i}\boldsymbol{q}\cdot[\boldsymbol{x}_u-\boldsymbol{x}_v])\rangle_0 \tag{4.39}$$

which evaluates to

$$C_n(\boldsymbol{k},\boldsymbol{q};\mu)=Z_0\exp(-\boldsymbol{k}^2G_{rp}-\boldsymbol{q}^2G_{uv}+\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{q}P_{uv;rp}) \tag{4.40}$$

where $Z_0=\langle\exp(-\mu\,\mathrm{tr}\,\mathcal{T})\rangle_0$, and

$$P_{uv;rp}(\mu)=A^{-1}_{ur}+A^{-1}_{vp}-A^{-1}_{up}-A^{-1}_{vr}+\frac{1}{4c}t_{uv}t_{rp}. \tag{4.41}$$

The integrand in the second term on the right-hand side of equation (4.38) is $C_n(\boldsymbol{k},\boldsymbol{q};0)$; the integrand in the third term is $C_n(\boldsymbol{k},\boldsymbol{0};0)$. We also find

$$P_{uv;rp}(0)=\tfrac{1}{2}(g_{ur}+g_{vp}-g_{up}-g_{vr}) \tag{4.42}$$

by the definition (4.10) for g_{uv}, and noting that $c^{-1}t_{uv}t_{rp}|_{\mu=0}=0$, by equation (4.24).

We digress briefly here for a look at the tethered membranes [23]. The expression for $P_{uv;rp}(0)$ above is to be compared with an analogous expression in the study of tethered membranes involving the Coulomb potential $C_D(\boldsymbol{x}-\boldsymbol{x}')$ in the 'internal' D-dimensional space (equation (3.8) of [23]):

$$A_D(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x},\boldsymbol{x}')=C_D(\boldsymbol{x}_1-\boldsymbol{x})+C_D(\boldsymbol{x}_2-\boldsymbol{x}')-C_D(\boldsymbol{x}_1-\boldsymbol{x}')-C_D(\boldsymbol{x}_2-\boldsymbol{x}). \tag{4.43}$$

$D=1$ for polymers and $D=2$ for surfaces. It is clear from equations (4.42) and (4.43) that we can identify (in the sense described below) $g_{uv}(0)$ with $(4/K)C_{D=1}(\boldsymbol{x}_u-\boldsymbol{x}_v)$. One can show that the term $\mu\,\mathrm{tr}\,\mathcal{T}$ defined by equation (2.2) introduces connections between a particular monomer and other monomers that are not its nearest neighbours along the chain. Equivalently, one can say that the effect of μ in $g_{uv}(\mu)$ is to introduce correlations which lead to the collapse of the chain, as we saw at the end of section 3. The generalization of $C_D(\boldsymbol{x})$ is effected by increasing the value of D from 1. Since $C_D(\boldsymbol{x})\propto|\boldsymbol{x}|^{2-D}$ [23], we see that, for $1<D<2$, $C_D(\boldsymbol{x})$ corresponds to objects of smaller overall size than those described by $C_{D=1}(\boldsymbol{x})$, for the same given contour size. More precisely, the fractal dimension, $d_{\rm f}=2D/(2-D)$, is two for the random walk ($D=1$) and infinite for a surface ($D=2$) [23]. For $D>1$, each 'monomer' in the membrane is connected to more neighbours than is the case for the linear topology $D=1$. Therefore, $g_{uv}(\mu)$, $\mu>0$, is to be identified with $C_D(\boldsymbol{x})$, $D>1$.

Substituting $C_n(\boldsymbol{k},\boldsymbol{q};0)$ and $C_n(\boldsymbol{k},0;0)$ from equation (4.40) into equation (4.38), and taking $-\nabla_q^2|_{\boldsymbol{q}=0}$, we obtain the end-to-end distance between monomers u and v as

$$R^2_{uv}=\frac{d}{2}g_{uv}(0)+b\ell^4\int\mathrm{d}r\,\mathrm{d}p\,[P(0)]^2\int_{\boldsymbol{k}}\boldsymbol{k}^2\,\mathrm{e}^{-\frac{1}{4}k^2g_{rp}(0)} \tag{4.44}$$

where we suppressed the indices on $P_{uv;rp}(0)$. The end-to-end distance for the whole chain is obtained by setting $u = n$, $v = 1$, for which

$$P_{n1;rp}(0) = \frac{1}{2\gamma}[|r - p| + n(\delta_{nr} - \delta_{np})]. \tag{4.45}$$

The terms involving the Kronecker deltas do not contribute. The k-integral in equation (4.44) was evaluated in equation (4.26). This leads to

$$\int_{|r-p|>n_0}^{n} \mathrm{d}r\, \mathrm{d}p |r - p|^{-1-d/2} = 2\left(\frac{n^{d_3}}{d_2 d_3} - \int_0^{n_0} \mathrm{d}x\, x^{d_1}(n - x)\right) \tag{4.46}$$

where $d_k = k - d/2$. Rescaling $\ell^2 \to \ell^2/2$, $b \to b/2$, we finally obtain

$$\frac{R_{\mathrm{E}}^2}{R_{\mathrm{E}^0}^2} = 1 + \frac{z}{(2 - d/2)(3 - d/2)} \tag{4.47}$$

where $z = bL^{2-d/2}(2\pi)^{-d/2}$, and $R_{\mathrm{E}^0}^2 = Ld$ is the end-to-end distance of a Gaussian chain. The cut-off dependence given by the integral on the right-hand side of equation (4.46) has the structure obtained in [15]. The ϵ-expansion of equation (4.47) is

$$\frac{R_{\mathrm{E}}^2}{R_{\mathrm{E}^0}^2} = 1 + \frac{2}{\epsilon}\left(1 - \frac{\epsilon}{2}\right) z. \tag{4.48}$$

This, combined with the corresponding equation (4.37) for R_{G}^2, gives

$$\frac{R_{\mathrm{G}}^2}{R_{\mathrm{E}}^2} = \frac{1}{6}\left(1 - \frac{z}{12}\right) \tag{4.49}$$

which has been obtained in [8] and [15], and also by field-theoretic methods [24].

5. Conclusion

The usual approach in theoretical studies of long, flexible, polymers in a good solvent is to adopt either a discrete model or a continuous one. In the discrete approach, exemplified by [16, 22], the non-interacting part of the Hamiltonian, ensuring chain connectedness, is $\mathcal{H}_0^{\mathrm{disc}} = \gamma \sum_{i=1}^{n} (\boldsymbol{r}_i - \boldsymbol{r}_{i-1})^2$ (equation (2.1)); the associated (discrete) excluded volume interaction is modelled according to Domb [22]: $\mathcal{H}_{\mathrm{int}}^{\mathrm{disc}} = \prod_{i,j}[1 + \beta\delta^d(\boldsymbol{r}_i - \boldsymbol{r}_j)]$. On the other hand, the continuous approach, exemplified by [5, 8, 15], takes $\mathcal{H}_0^{\mathrm{cont}} = (d/2\ell)\int_0^L \mathrm{d}s[\mathrm{d}\boldsymbol{r}(s)/\mathrm{d}s]^2$ and the interaction part as $\mathcal{H}_{\mathrm{int}}^{\mathrm{cont}} = b\iint \mathrm{d}s\, \mathrm{d}s'\, \delta^d[\boldsymbol{r}(s) - \boldsymbol{r}(s')]$. In the present paper we have adopted a hybrid approach consisting of a *discrete* non-interacting chain part, $\mathcal{H}_\mu = \mu\,\mathrm{tr}\,\mathcal{T} + \mathcal{H}^{\mathrm{disc}}$ (equation (1.9)), of the Hamiltonian, and a *continuous* excluded volume interaction, $\mathcal{H}_{\mathrm{int}}^{\mathrm{cont}}$, due to Edwards [14].

By introducing the term $\mu\,\mathrm{tr}\,\mathcal{T}$ we were able to construct the (canonical) partition function for a discrete Gaussian chain. We express the result in terms of a hypergeometric function, which is subsequently used extensively throughout the paper. Using the model of Edwards for the excluded volume interaction, we derived dimensionally regularized expressions for R_{G}^2 and R_{E}^2, together with the cut-off dependence of [15]. In other words, the 'renormalization' of a discrete chain (equation (1.9)) and of a continuous one (modelled by $\mathcal{H}_0^{\mathrm{cont}}$), due to the excluded volume interaction $\mathcal{H}_{\mathrm{int}}^{\mathrm{cont}}$, turns out to be the same. This seems to be consistent with the finding in [16], viz, that one can derive from a discrete chain model results which are identical to those derived by sophisticated and elaborate renormalization techniques based on a continuous chain model.

The technique developed in this paper can be used to study the polymer at the θ-point, and the shape of a Gaussian chain. The latter will be pursued in a subsequent publication.

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Appendix. Evaluation of determinants

In this appendix we evaluate the determinant of the matrices $M_{ij}(\mu)$ (equation (3.1)) and $A_{ij}(\mu)$ (equation (4.12)), and express the results in terms of the hypergeometric function. $M_{ij}(\mu)$ can be diagonalized [13]. However, that approach only leads to a closed form expression for $\det \mathbf{M}$ in the limit $n \to \infty$. By using recursion relations for the determinants, as well as differentiation formulae, we derive closed form expressions for $\det \mathbf{M}$ and $\det \mathbf{A}$; they are Jacobi polynomials. Let us decompose $\det \mathbf{M}$ into tridiagonal forms so as to emphasize the random walk nature of the problem. We have

$$\det M_n = \det A_n - b \sum_{m=1}^{n} m\gamma^{n-m} D_{m-1}. \tag{A1}$$

This can be shown by evaluating $\det M_n$ for small n and generalizing the results. Here $\mathbf{A}$ is a tridiagonal matrix defined by

$$A_{ij} = \begin{cases} 2\gamma + a & i = j = 1, 2, \ldots, n-1 \\ \gamma + a & i = j = n \\ -\gamma & |i - j| = 1 \\ 0 & \text{otherwise} \end{cases} \tag{A2}$$

and D_m denotes the determinant of the $m \times m$ Jacobi matrix

$$D_{ij} = \begin{cases} 2\gamma + a & i = j \\ -\gamma & |i - j| = 1 \\ 0 & \text{otherwise.} \end{cases} \tag{A3}$$

It is straightforward to show that

$$\det A_n = (\gamma + a) D_{n-1}(x) - \gamma^2 D_{n-2}(x) \qquad x = 2\gamma + a \tag{A4}$$

so that all we need for the evaluation of $\det \mathbf{M}$ in (A1) is $D_m(x)$, which obeys the recursion relation

$$D_m(x) = x D_{m-1}(x) - \gamma^2 D_{m-2}(x) \tag{A5}$$

with the boundary conditions $D_0 = 1$, $D_{-k} = 0 (k > 0)$. $D_m(x)$ can be written as [25]

$$D_m(x) = \frac{\gamma^{m+1}}{\sqrt{x^2 - 4\gamma^2}} (v_+^{m+1} - v_-^{m+1}) \tag{A6}$$

where

$$v_\pm = \frac{1}{2\gamma} (x \pm \sqrt{x^2 - 4\gamma^2}) \tag{A7}$$

are the roots of the quadratic equation $v^2 - vx + \gamma^2 = 0$.

Using the form (A6), the sum in (A1) becomes

$$\sum_{m=1}^{n} m\gamma^{n-m} D_{m-1} = \frac{\gamma^n}{\sqrt{x^2 - 4\gamma^2}} \left[v_+ \frac{\partial}{\partial v_+} \sum_{m=1}^{n} v_+^m - v_- \frac{\partial}{\partial v_-} \sum_{m=1}^{n} v_-^m \right]. \tag{A8}$$

Since

$$\sum_{m=1}^{n} v^m = \frac{v^{n+1} - v}{v - 1} \tag{A9}$$

we find

$$v_+ \frac{\partial}{\partial v_+} \sum_{m=1}^{n} v_+^m = \frac{1}{(v_+ - 1)^2}[n v_+^{n+2} - (n+1)v_+^{n+1} + v_+] \tag{A10}$$

and an analogous expression for v_-. Using these in the square bracket of equation (A8), and noting that $v_+ v_- = 1$, the sum becomes

$$\sum_{m=1}^{n} m\gamma^{n-m} D_{m-1} = \frac{n}{a}[(a+\gamma)D_{n-1} - \frac{\gamma}{a}D_{n-1} - \gamma^2 D_{n-2}]. \tag{A11}$$

Combining this with $\det A_n$ given by equation (A4) leads to

$$\det M_n = \frac{\gamma}{n} D_{n-1}(x) \qquad x = 2\gamma + a. \tag{A12}$$

Let us express $\det \mathbf{M}$ in terms of the hypergeometric function. We note a special case of the hypergeometric function [26]

$${}_2F_1(-n, n; \tfrac{1}{2}; -z^2) = \tfrac{1}{2}[(\sqrt{1+z^2} + z)^{2n} + (\sqrt{1+z^2} - z)^{2n}]. \tag{A13}$$

Differentiating both sides of equation (A13) with respect to z^2, using the property [26]

$$\frac{\mathrm{d}}{\mathrm{d}x}\,{}_2F_1(a, b; c; x) = \frac{ab}{c}\,{}_2F_1(a+1, b+1; c+1; x) \tag{A14}$$

we obtain

$${}_2F_1(n+1, -n+1; \tfrac{3}{2}; -z^2) = \frac{1}{4nz\sqrt{1+z^2}}[(\sqrt{1+z^2} + z)^{2n} - (\sqrt{1+z^2} - z)^{2n}] \tag{A15}$$

which is related to D_n in equation (A6). We show this as follows. Since $x = 2\gamma + a$ (equation (A4)), and $a = \mu/n$, we find $x \pm \sqrt{x^2 - 4\gamma} = 2\gamma(z \pm \sqrt{1+z^2})^2$, where we have used $z^2 = \mu/(4n\gamma)$. Substituting into equation (A6), we obtain

$$D_{n-1}(z) = \frac{\gamma^{n-1}}{4z\sqrt{1+z^2}}[(\sqrt{1+z^2} + z)^{2n} - (\sqrt{1+z^2} - z)^{2n}]. \tag{A16}$$

Comparing with equation (A15), we conclude

$$D_{n-1}(z) = n\gamma^{n-1}\,{}_2F_1(-n+1, n+1; \tfrac{3}{2}; -z^2). \tag{A17}$$

Substituting into equation (A12), we obtain

$$\det M_n(\mu) = \gamma^n\,{}_2F_1(-n+1, n+1; \tfrac{3}{2}; -z^2) \qquad z^2 = \mu/(4n\gamma). \tag{A18}$$

Apart from the factor $\Gamma(3/2)\Gamma(n)/\Gamma(n+1/2)$, the right-hand side of equation (A18) is the Jacobi polynomial $P_{n-1}^{(1/2,1/2)}(1+2z^2)$ [21]. It is also equivalent to the Gegenbauer polynomial $(1/n)C_{n-1}^1(1+2z^2)$ [21].

$\mathrm{Det}\,\mathbf{A}$ can also be expressed as a hypergeometric function. Substitution of equation (A17) into (A4) gives

$$\det A_n = \gamma^n[n(1+4z^2)\,{}_2F_1(-n+1, n+1; \tfrac{3}{2}; -z^2) - (n-1)\,{}_2F_1(-n+2, n; \tfrac{3}{2}; -z^2)]. \tag{A19}$$

The right-hand side can be simplified by using the form (A15) for the hypergeometric function and noting that the second hypergeometric function in the square bracket of equation (A19) can be obtained from the first by the replacement $n \to n-1$. The result is

$$\det A_n = \frac{\gamma^n}{2\sqrt{1+z^2}}[(\sqrt{1+z^2}+z)^{2n+1} + (\sqrt{1+z^2}-z)^{2n+1}]. \tag{A20}$$

Comparison with the form

$$ {}_2F_1(-n, n+1; \tfrac{1}{2}; -w) = \frac{1}{2\sqrt{1+w}}[(\sqrt{1+w}+\sqrt{w})^{2n+1} + (\sqrt{1+w}+\sqrt{w})^{-2n-1}] \qquad |w| < 1 \tag{A21}$$

([27], equation (7.3.10)) leads to

$$\det A_n = \gamma^n \, {}_2F_1(-n, n+1; \tfrac{1}{2}; -z^2) \tag{A22}$$

since $(\sqrt{1+w}+\sqrt{w}) = (\sqrt{1+w}-\sqrt{w})^{-1}$.

Finally, we list several useful properties of the hypergeometric function. Since $-n+1$ is a negative integer, ${}_2F_1(-n+1, n+1; \frac{3}{2}; -z^2)$ is a polynomial of degree $n-1$; it is (except for a constant) the Jacobi polynomial $P_{n-1}^{(\alpha,\beta)}(x)$, with $\alpha = \beta = \frac{1}{2}$ and $x = 1+2z^2$ [21]. For $z < 1$ the hypergeometric function can be expressed as a (convergent) power series [6, 27]

$$ {}_2F_1(a, b; c; z) = \sum_{k=0}^{\infty} \frac{(a)_k (b)_k}{(c)_k} \frac{z^k}{k!} \qquad |z| < 1 \tag{A23}$$

where $(\alpha)_k \equiv \Gamma(\alpha+k)/\Gamma(\alpha) = \alpha(\alpha+1)\ldots(\alpha+k-1), k = 1, 2, \ldots,$ denotes the Pochhammer symbol. It follows that ${}_2F_1(a, b; c; 0) = 1$. We also note the symmetry ${}_2F_1(a, b; c; z) = {}_2F_1(b, a; c; z)$ with respect to interchange of the arguments a and b.

In the limit $n \to \infty (z < 1)$ one can use the hypergeometric series in equation (A23) to obtain

$$ {}_2F_1(-n, n+1; \tfrac{1}{2}; -z^2) \to \cosh(2nz)$$
$$ {}_2F_1(-n+1, n+1; \tfrac{3}{2}; -z^2) \to \frac{\sinh(2nz)}{2nz} \qquad n \to \infty \tag{A24}$$

after a bit of algebra. By equation (A15),

$$ {}_2F_1(-n+1, n+1; \tfrac{3}{2}; -1) = \frac{(\sqrt{2}+1)^{2n}}{4\sqrt{2}n}\left[1 - \frac{1}{(\sqrt{2}+1)^{4n}}\right]. \tag{A25}$$

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